PATENT ABSTRACTS OF JAPAN

(11) Publication number:

10-101661

(43) Date of publication of application: 21.04.1998

(51)Int.Cl.

C07D303/20 // C08F 20/58

(21)Application number : 08-254443

(71)Applicant: KURARAY CO LTD

(22)Date of filing:

26.09.1996

(72)Inventor: ANDO YOSHINORI

FUJIWARA NAOKI

(54) ACRYLAMIDE DERIVATIVE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a new acrylamide that has excellent compatibility with polymers regardless of kinds and chain length of polymers, is useful as modifier or denaturant for polymers, and can be polymerized single or copolymerized with other monomers.

SOLUTION: This acrylamide of formula I (R1 and R2 are H, methyl; (n) is 1-6), for example, N-(glycydiloxymethyl) acrylamide, is obtained be heating preferably 1mol of an acrylamide derivative of formula II (R3 is H or a lower alkyl) and 0.8-200mol of an epoxy alcohol of formula III to react with each other in the presence of 0.001-100mol of an acidic substance, such as phosphoric acid, and 0.0001-0.1mol of a polymerization inhibitor, such as hydroquinone monoether, at 20-100°C.

$$R^1$$
 N
 CH_2
 OR^3

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than

the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the acrylamide derivative containing an epoxy group. This acrylamide derivative is used for adhesives, the raw material for coatings, etc. as reforming of a polymer, and a modifier.

[0002]

[Description of the Prior Art] Conventionally, the acrylamide compound (refer to JP,2-51550,B) which can be used as reforming of a polymer and a modifier and which contains the ring permuted by N-glycidyl permutation amide compound (refer to JP,2-39505,B), the N-2-methyl glycidyl permutation amide compound (refer to JP,3-72624,B), and the glycidyloxy radical as an acrylamide derivative containing an epoxy group was known.

[0003]

[Problem(s) to be Solved by the Invention] Since the above-mentioned N-glycidyl permutation amide compound and the N-2-methyl glycidyl permutation amide compound were restricted to the compound which contains the short glycidyl group and 2-methyl glycidyl group of chain length, respectively, and since the acrylamide compound given in JP,2-51550,B contained the ring, when it was used as reforming of a polymer, and a modifier, depending on the class of polymer, it had the trouble that compatibility was bad. Therefore, offer of the polymerization nature monomer used as reforming of a polymer and a modifier which shows the class of polymer and the compatibility which was excellent irrespective of chain length was called for.

[0004]

[Means for Solving the Problem] It is a general formula (1) as a result of the wholeheartedly examination about the acrylamide derivative which can be made to be able to carry out a polymerization independently by itself, or can carry out copolymerization to various polymerization nature monomers, such as ethylene, a propylene, styrene, a butadiene, a methyl acrylate, a methyl methacrylate, and vinyl acetate, by the polymerization nature monomer containing reforming of a polymer, and the epoxy group as a functional group used for denaturation.

[0005]

[0006] (-- R1 and R2 express a hydrogen atom or a methyl group among a formula, and n expresses the integer of 1 to 6.) -- the acrylamide derivative (this may be hereafter called acrylamide derivative (1) for short) list shown -- general formula (2) [0007]

[Formula 10]
$$\begin{array}{ccc}
R^1 & H \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& & \\
& &$$

[0008] (-- R1 is as said definition among a formula, and R3 expresses a hydrogen atom or a low-grade alkyl group.) -- the acrylamide derivative (this may be hereafter called an acrylamide derivative (2) for short) shown -- general formula (3)

[0009]

[Formula 11]

$$HO$$
 CH_2
 n
 (3)

[0010] (-- R2 and n are as said definition among a formula.) -- general formula (1) by making it react with the epoxy alcohol (for this to be hereafter called epoxy alcohol (3) for short) shown [0011]

[0012] (-- R1, R2, and n are as said definition among a formula.) -- the manufacture approach of the acrylamide derivative shown, and general formula (2) [0013]

[Formula 13]

$$\begin{array}{c|c}
R^1 & H \\
N & CH_2 & OR^3
\end{array} (2)$$

[0014] (-- R1 and R3 are as said definition among a formula.) -- the acrylamide derivative shown -- general formula (4)

[0015]

[Formula 14]

$$HO$$
 (CH_2)
 n
 (4)

[0016] (-- R2 and n are as said definition among a formula.) -- making it react with the alcohol (for this to be hereafter called alcohol (4) for short) shown -- general formula (5) [0017]

[Formula 15]
$$\begin{array}{cccc}
R^1 & H & R^2 \\
N & CH_2 & CH_2 & (5)
\end{array}$$

[0018] (-- R1, R2, and n are as said definition among a formula.) -- general formula (1) by considering as the acrylamide derivative (this being hereafter called an acrylamide derivative (5) for short) shown, and subsequently carrying out epoxidation

[0019]

[Formula 16]
$$\begin{array}{cccc}
R^1 & H & R^2 \\
N & CH_2 & CH_2 & CH_2 & CH_2
\end{array}$$
(1)

[0020] (-- R1, R2, and n are as said definition among a formula.) -- the manufacture approach of the acrylamide derivative shown was found out and this invention was completed. [0021]

[Embodiment of the Invention] It sets to said general formula (2), and is R3. As a low-grade alkyl group expressed, the alkyl group of the carbon numbers 1-5, such as a methyl group, an ethyl group, a propyl group, butyl, an isopropyl group, and t-butyl, is mentioned.

[0022] Next, the manufacture approach of the acrylamide derivative (1) by making an acrylamide derivative (2) react with epoxy alcohol (3) first is explained. It is convertible for an acrylamide derivative (1) by only heating an acrylamide derivative (2) and epoxy alcohol (3), and making them react, or making it heat and react to the bottom of existence of the acid. The reaction temperature in the case of only heating is within the limits of about 100-180 degrees C, and the reaction temperature in the case of heating under existence of the acid is within the limits of about 20-100 degrees C. the amount of an acrylamide derivative (2) and the epoxy alcohol (3) used -- acrylamide derivative (2) 1 mol -- receiving -- epoxy alcohol (3) -- the range of about 0.8-200 mols is desirable.

[0023] As usable acid, Lewis acid, such as salts, such as organic acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, and a phosphoric acid, a formic acid, an acetic acid, oxalic acid, and p-toluenesulfonic acid, p-toluenesulfonic-acid pyridinium, and an ammonium chloride, a zinc chloride, and an aluminum chloride, acid ion exchange resin, etc. are used. Although the amount of the acid used changes with properties of the acid to be used, the range of about 0.001-100 mols is usually desirable to acrylamide derivative (2) 1 mol. Although it is also possible to perform a reaction in a solvent, as a solvent, hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, dioxane, ethylene glycol wood ether, ethylene glycol diethylether, diethylene-glycol wood ether, and diethylene-glycol diethylether, a hexane, a heptane, benzene, toluene, and a xylene, etc. are used. The amount of the solvent used usually has the desirable range of about 1 - 100 time weight to an acrylamide derivative (2). As for a reaction, it is desirable to carry out under coexistence of polymerization inhibitor. As polymerization inhibitor, phenol system polymerization inhibitor, such as the hydroquinone monomethyl ether, etc. is used. The amount of the polymerization inhibitor used usually has the desirable range of about 0.0001-0.1 mols to acrylamide derivative (2) 1 mol. Moreover, in order to press down a polymerization, it is desirable to also make it react, blowing air.

[0024] Isolation and purification from the reaction mixture of an acrylamide derivative (1) are performed like the approach used in isolation and purification of the usual organic compound. For example, a reaction mixture is opened in saturation sodium bicarbonate water, and organic solvents, such as ethyl acetate, diethylether, and a methylene chloride, extract. An extract is dried after saturation brine subsequently washes, water and, and it condenses, a rough product is obtained, and a chromatography etc. refines if needed.

[0025] Next, an acrylamide derivative (2) is made to react with alcohol (4), an acrylamide derivative (5) is obtained, and how to carry out epoxidation of this and to manufacture an acrylamide derivative (1) is explained. An acrylamide derivative (5) can be obtained by only heating an acrylamide derivative (2) and alcohol (4), and making them react, or making it heat and react to the bottom of existence of the

acid. The reaction temperature in the case of only heating is within the limits of about 100-180 degrees C, and the reaction temperature in the case of heating under existence of the acid is within the limits of about 20-100 degrees C. the amount of an acrylamide derivative (2) and the alcohol (4) used -- acrylamide derivative (2) 1 mol -- receiving -- alcohol (4) -- the range of about 0.8-200 mols is desirable.

[0026] As usable acid, Lewis acid, such as salts, such as organic acids, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, and a phosphoric acid, a formic acid, an acetic acid, oxalic acid, and p-toluenesulfonic acid, p-toluenesulfonic-acid pyridinium, and an ammonium chloride, a zinc chloride, and an aluminum chloride, acid ion exchange resin, etc. are used. Although the amount of the acid used changes with properties of the acid to be used, the range of about 0.001-100 mols is usually desirable to acrylamide derivative (2) 1 mol. Although it is also possible to perform a reaction in a solvent, as a solvent, hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, dioxane, ethylene glycol wood ether, ethylene glycol diethylether, diethylene-glycol wood ether, and diethylene-glycol diethylether, a hexane, a heptane, benzene, toluene, and a xylene, etc. are used. The amount of the solvent used usually has the desirable range of about 1 - 100 time weight to an acrylamide derivative (2). As for a reaction, it is desirable to carry out under coexistence of polymerization inhibitor. As polymerization inhibitor, phenol system polymerization inhibitor, such as the hydroquinone monomethyl ether, etc. is used. The amount of the polymerization inhibitor used usually has the desirable range of about 0.0001-0.1 mols to acrylamide derivative (2) 1 mol. Moreover, in order to press down a polymerization, it is desirable to also make it react, blowing air.

[0027] Isolation and purification from the reaction mixture of an acrylamide derivative (5) are performed like the approach used in isolation and purification of the usual organic compound. For example, a reaction mixture is opened in saturation sodium bicarbonate water, and organic solvents, such as ethyl acetate, diethylether, and a methylene chloride, extract. An extract is dried and condensed after saturation brine subsequently washes, water and, a rough product is obtained, and it is carried out by refining with a chromatography etc. if needed.

[0028] An acrylamide derivative (5) is convertible for an acrylamide derivative (1) by carrying out epoxidation using a peroxy acid, oxygen, a peroxide, etc.

[0029] m-chloro perbenzoic acid, a peracetic acid, etc. are mentioned as a peroxy acid. The amount of the peroxy acid used has the desirable range of about 1-10 mols to acrylamide derivative (5) 1 mol. It is desirable to perform a reaction in a solvent and a methylene chloride, chloroform, an acetic acid, water, these mixed solvents, etc. are used as a solvent. The amount of the solvent used usually has the desirable range of about 1 - 100 time weight to an acrylamide derivative (5). Moreover, in order to neutralize the generated acid, it is also possible to add sodium bicarbonate water. The amount of the sodium bicarbonate water used has the desirable water solution which melted about 1-10-mol sodium bicarbonate in the water of weight about ten to 100 times to sodium bicarbonate to one mol of usually used peroxy acids. A reaction can be performed under inert gas ambient atmospheres, such as nitrogen. Reaction temperature is [about]. -It is the temperature within the limits of 80-30 degrees C. [0030] Next, use of oxygen is explained, nickel (dmp)2 etc. -- epoxidation of the acrylamide derivative (5) can be carried out with oxygen or air to the bottom of existence of aldehydes, such as a metal catalyst and isobutyraldehyde, and an acrylamide derivative (1) can be obtained. Although the amount of the metal catalyst used changes also with classes of catalyst to be used, its range of about 0.0001-0.5 mols is desirable to acrylamide derivative (5) 1 mol. The amount of the aldehyde used has desirable about 1-10 mols to acrylamide derivative (5) 1 mol. A reaction is performed under the ambient atmosphere of oxygen or air. It is desirable to perform a reaction in a solvent and halogenated hydrocarbon solvents, such as a methylene chloride, chloroform, or 1,2-dichloroethane, are used as a solvent. The amount of the solvent used usually has the desirable range of about 1 - 100 time weight to an acrylamide derivative (5). Reaction temperature is the temperature within the limits of about 0-80 degrees C.

[0031] A peroxide is also usable, for example, the preparation agent from a hydrogen peroxide, a hydrogen peroxide, the preparation agent from an acetonitrile and a hydrogen peroxide, and a

benzonitrile etc. is mentioned.

[0032] Thus, isolation and purification from the reaction mixture of the acrylamide derivative (1) obtained are performed like the approach used in isolation and purification of the usual organic compound. For example, a reaction mixture is opened in saturation sodium bicarbonate water, and organic solvents, such as ethyl acetate, diethylether, and a methylene chloride, extract. An extract is dried and condensed after saturation brine subsequently washes, a saturation sodium-thiosulfate water solution, saturation sodium bicarbonate water, water, and, a rough product is obtained, and it is carried out by refining with a chromatography etc. if needed.

[0033] In addition, an acrylamide derivative (5) is compoundable also by making acrylamide or methacrylamide react to the bottom of existence of the acid with formalin and alcohol (4). [0034]

[Example] Hereafter, this invention is not limited by these examples although an example explains this invention still more concretely.

[0035] It agitated at 50 degrees C for 5.5 hours, putting in and carrying out air bubbling of N-methylol acrylamide 10g, hydroquinone monomethyl ether 40mg, glycidol 25.6g, and the 48.5mg of the phosphoric acids to example 1 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(glycidyl oxymethyl) acrylamide 1.5g which has the following physical-properties value was obtained.

[0036] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [2.63 (dd, J = 3.0 or 4.9Hz 1H),] 2.80 (dd, J = 3.8 or 4.9Hz, 1H), 3.12-3.18 (m, 1H), 3.41 (dd, J = 11.8 or 6.3Hz, 1H) 3.91 (dd, J = 11.8 or 3.0Hz, 1H), 4.79-4.91 (m, 2H), 5.71 (d, J= 10.1Hz, 1H), 6.19 (dd, J = 10.1 or 16.9Hz, 1H), 6.32 (d, J= 16.9Hz, 1H), 7.03 (brs, 1H) [0037] It agitated at 100 degrees C for 8 hours, putting in and carrying out air bubbling of N-(t-butoxy methyl) acrylamide 3g, hydroquinone monomethyl ether 12.1mg, glycidol 4.9g, and the 30mg of the p-toluenesulfonic acid to example 2 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(glycidyl oxymethyl) acrylamide 1.3g which has the same physical-properties value as what was obtained in the example 1 was obtained.

[0038] It agitated at 80 degrees C for 3 hours, putting in and carrying out air bubbling of 7 and 8-epoxy octane-1-all-ones g and hydroquinone monomethyl ether 3.4mg, N-methylol acrylamide 842mg, ethylene glycol wood ether 3ml, and the 4mg of the phosphoric acids to example 3 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(7, 8-epoxy octyl oxymethyl) acrylamide 110mg which has the following physical-properties value was obtained.

[0039] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [1.22-1.64 (m, 10H),] 2.46 (dd, J = 3.4 or 3.8Hz, 1H) 2.74 (dd, J = 3.8 or 3.8Hz, 1H), 2.88 (brs, 1H) 3.50 (t, J= 6.3Hz, 2H), 4.81 (d, J= 7.2Hz, 2H), 5.70 (d, J= 9.7Hz, 1H), 6.15 (dd, J = 9.7 or 16.9Hz, 1H), 6.34 (d, J= 16.9Hz, 1H), 6.67 (brs, 1H) [0040] It agitated at 50 degrees C for 6 hours, putting in and carrying out air bubbling of allyl alcohol 20.1g, hydroquinone monomethyl ether 49mg, N-methylol acrylamide 10g, and the 61mg of the phosphoric acids to example 4 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(aryloxymethyl)

acrylamide 11.3g which has the following physical-properties value was obtained. [0041] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [4.06 (d, J= 6.3Hz, 2H),] 4.82 (d, J= 6.3Hz, 2H) 5.18 (d, 10.1Hz, 1H), 5.28 (d, J= 16.9Hz, 1H), 5.71 (d, J= 10.1Hz, 1H), 5.82-5.98 (m, 1H), 6.16 (dd, J= 10.1 or 16.9Hz, 1H), 6.34 (d, J= 16.9Hz, 1H), 6.88 (brs, 1H) [0042] N-(aryloxymethyl) acrylamide 1g, 25ml of methylene chlorides, and sodium bicarbonate water (it prepares from 0.8g of sodium hydrogenearbonates and 25ml of water) were put into example 5 reactor, and it agitated under the iced water cold. 2.1g of m-chloro perbenzoic acids was added to reaction mixture, and it agitated for 30 minutes, cooled. Reaction mixture was opened in water and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(glycidyl oxymethyl) acrylamide 85mg which has the same physical-properties value as what was obtained in the example 1 was obtained.

[0043] It agitated at 80 degrees C for 6 hours, putting in and carrying out air bubbling of 7-octene-1-all 30g, hydroquinone monomethyl ether 113mg, N-methylol acrylamide 42.6g, and the 138mg of the phosphoric acids to example 6 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(7-OKUTE nil oxymethyl) acrylamide 17.3g which has the following physical-properties value was obtained.

[0044] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [1.28-1.50 (m, 6H),] 1.55-1.69 (m, 2H), 2.02-2.18 (m, 2H), 3.56 (t, J=5.5Hz, 2H) 4.87 (d, J=6.3Hz, 2H), 5.00 (d, J=8.9Hz, 1H) 5.04 (d, J=14.3Hz, 1H), 5.78 (d, J=10.5Hz, 1H), 5.75-5.95 (m, 1H), 6.22 (dd, J=10.5 or 17.7Hz, 1H), 6.42 (d, J=17.7Hz, 1H), 6.73 (brs, 1H) [0045] N-(7-OKUTE nil oxymethyl) acrylamide 5g and 50ml of methylene chlorides were put into example 7 reactor, and it agitated under the iced water cold. 8.2g of m-chloro perbenzoic acids was added to reaction mixture, and it extracted using the methylene chloride. In the saturation sodium-thiosulfate water solution, the extract was condensed under reduced pressure, after saturation sodium bicarbonate water and saturation brine having washed subsequently and drying using anhydrous sodium sulfate, washing and. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(7, 8-epoxy octyl oxymethyl) acrylamide 1.7g which has the same physical-properties value as what was obtained in the example 3 was obtained.

[0046] It agitated at 80 degrees C for 10.5 hours, putting in and carrying out air bubbling of 3-methyl-3-butene-1-all 20g, hydroquinone monomethyl ether 111mg, N-methylol acrylamide 30.5g, and the 136mg of the phosphoric acids to example 8 reactor. Reaction mixture was opened in saturation sodium bicarbonate water after radiationnal cooling, and it extracted using ethyl acetate. After saturation brine's having washed the extract and drying using anhydrous sodium sulfate, it condensed under reduced pressure. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(3-methyl-3-butenyl oxymethyl) acrylamide 20.4g which has the following physical-properties value was obtained.

[0047] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [1.80 (s, 3H),] 2.34 (t, J= 5.1Hz, 2H) 3.70 (t, J= 5.1Hz, 2H), 4.78 (s, 1H), 4.85 (s, 1H), 4.88 (d, J= 7.2Hz, 2H), 5.78 (d, J= 10.1Hz, 1H), 6.22 (dd, J= 10.5 or 17.3Hz, 1H), 6.41 (d, J= 17.3Hz, 1H), 6.77 (brs, 1H) [0048] N-(3-methyl-3-butenyl oxymethyl) acrylamide 5g and 50ml of methylene chlorides were put into example 9 reactor, and it agitated under the iced water cold. 6.1g of m-chloro perbenzoic acids was added to reaction mixture, and it agitated for 50 minutes, cooled. Reaction mixture was opened in saturation sodium bicarbonate water, and it extracted using ethyl acetate. In the saturation sodium-thiosulfate water solution, the extract was condensed under reduced pressure, after saturation sodium bicarbonate water and saturation brine having washed subsequently

and drying using anhydrous sodium sulfate, washing and. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide 2.4g which has the following physical-properties value was obtained. [0049] 1 H-NMR Spectrum (270MHz)

delta (ppm in CDCl3:TMS): [1.33 (s, 3H),] 1.74 - 1.93 (m, 2H) and 2.58 (d, J= 3.4, 1H) -- 2.67 (d, J= 3.4, 1H) 3.62 (t, J= 5.1Hz, 2H), 4.80 (d, J= 5.9Hz, 2H), 5.73 (d, J= 9.3Hz, 1H), 6.15 (dd, J= 9.3 or 17.7Hz, 1H), 6.35 (d, J= 17.7Hz, 1H), 6.67 (brs, 1H) [0050] N-(3-methyl-3-butenyl oxymethyl) acrylamide 2g and 20ml of methylene chlorides were put into the reactor under example 10 nitrogen, and it agitated under the iced water cold. 85ml (1 mol/L) of peracetic acids was dropped at reaction mixture, and in addition, it agitated for 25 hours, cooled. Reaction mixture was opened in 3-N sodium-hydroxide water solution, and it extracted using ethyl acetate. In the saturation sodium-thiosulfate water solution, the extract was condensed under reduced pressure, after saturation sodium bicarbonate water and saturation brine having washed subsequently and drying using anhydrous sodium sulfate, washing and. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide 1.1g which has the same physical-properties value as what was obtained in the example 9 was obtained.

[0051] N-(3-methyl-3-butenyl oxymethyl) acrylamide 2g, nickel(dmp)2 155mg, isobutyraldehyde 1.8g, and 1,2-dichloroethane 8ml were put into the reactor under example 11 oxygen, and it agitated at the room temperature for 3 hours. Reaction mixture was opened in saturation sodium bicarbonate water, and it extracted using ethyl acetate. In the saturation sodium-thiosulfate water solution, the extract was condensed under reduced pressure, after saturation sodium bicarbonate water and saturation brine having washed subsequently and drying using anhydrous sodium sulfate, washing and. Separation purification of the concentration liquid was carried out using the silica gel column chromatography, and N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide 521mg which has the same physical-properties value as what was obtained in the example 9 was obtained.

[0052] 1.94g was taught for N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide, and 540g and 60g of methanols were taught to the 11. polymerization tank equipped with preparation opening and the pump for the example reflux condenser of reference, an agitator, a thermometer, nitrogen installation tubing, and adding after mixing liquid for vinyl acetate. When it warmed after carrying out the nitrogen purge of the inside of a system, agitating polymerization liquid, and it became 60-degree C constant temperature, 0.2g of 2 and 2-azobisisobutyronitrils was added, and the polymerization was started. The polymerization was performed carrying out continuation addition of the 10% methanol solution of N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide analyzing the solid content concentration in a system from a polymerization initiation time. The polymerization was suspended by cooling a polymerization tank 3 hours after. The addition of N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide of the time of a polymerization halt was 7.23g, and the solid content concentration at the time of a polymerization halt was 44.6%. The obtained polymerization paste was dropped into n-hexane and the polymerization object was deposited. Next, the polymerization object was dissolved in the acetone, and after carrying out reprecipitation purification actuation of making it depositing in n-hexane, 3 times, it dissolved in the acetone again. Subsequently, this was dropped at distilled water, after carrying out boiling purification, it dried at 60 degrees C and purification polyvinyl acetate was obtained. The viscosity average polymerization degree (P) searched for by the degree type from the limiting viscosity [eta] (g/dl) measured at 30 degrees C among the acetone about this polyvinyl acetate was 2900. P= ([eta] x103 / 7.94) (1/0.62). 1 The epoxy group content of N-(3 and 4-epoxy-3-methylbutyl oxymethyl) acrylamide origin computed from H-NMR (inside of 270MHz and deuteration chloroform) was 2.0-mol %.

[Effect of the Invention] The polymerization of the acrylamide derivative shown by the general formula (1) offered by this invention can be carried out independently in itself, or it can carry out copolymerization to polymerization nature monomers, such as ethylene, a propylene, styrene, a butadiene, a methyl acrylate, a methyl methacrylate, and vinyl acetate. Since the copolymer obtained contains an epoxy group, it can be used as useful reforming of this copolymer, and a modifier.

Therefore, this copolymer is usable for broad applications, such as adhesives and a raw material for coatings.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] General formula (1)

[Formula 1]

$$\begin{array}{c|c}
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\
 & & \\$$

(R1 and R2 express a hydrogen atom or a methyl group among a formula, and n expresses the integer of 1 to 6.) The acrylamide derivative shown.

[Claim 2] General formula (2)

[Formula 2]

$$\begin{array}{c|c}
R^1 & H \\
\hline
N & CH_2
\end{array}$$
(2)

(-- R1 expresses a hydrogen atom or a methyl group among a formula, and R3 expresses a hydrogen atom or a low-grade alkyl group.) -- the acrylamide derivative shown -- general formula (3) [Formula 3]

$$HO \leftarrow \begin{pmatrix} CH_2 \end{pmatrix}_{\mathbf{n}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

(-- R2 expresses a hydrogen atom or a methyl group among a formula, and n expresses the integer of 1 to 6.) -- general formula (1) by making it react with the epoxy alcohol shown

(-- R1, R2, and n are as said definition among a formula.) -- the manufacture approach of the acrylamide derivative shown.

[Claim 3] General formula (2)

[Formula 5]

$$\begin{array}{c|c}
R^1 & H \\
N & CH_2
\end{array}$$

$$\begin{array}{c}
OR^3
\end{array}$$
(2)

(-- R1 expresses a hydrogen atom or a methyl group among a formula, and R3 expresses a hydrogen atom or a low-grade alkyl group.) -- the acrylamide derivative shown -- general formula (4) [Formula 6]

$$R^2$$
 CH_2
 n
 (4)

(-- R2 expresses a hydrogen atom or a methyl group among a formula, and n expresses the integer of 1 to 6.) -- making it react with the alcohol shown -- general formula (5)

[Formula 7]
$$\begin{array}{cccc}
R^1 & H & R^2 \\
N & CH_2 & CH_2 & (5)
\end{array}$$

(-- R1, R2, and n are as said definition among a formula.) -- general formula (1) by considering as the acrylamide derivative shown and subsequently carrying out epoxidation [Formula 8]

$$\begin{array}{c|c}
R^{1} & H \\
N & CH_{2}
\end{array}$$

$$\begin{array}{c}
CH_{2} \\
N \\
\end{array}$$

$$\begin{array}{c}
R^{2} \\
CH_{2} \\
\end{array}$$

$$\begin{array}{c}
(1)
\end{array}$$

(-- R1, R2, and n are as said definition among a formula.) -- the manufacture approach of the acrylamide derivative shown.

[Translation done.]